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PREPRINT

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Surfaces and Coatings

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This paper was prepared for submittal to
Southwest Conference on Optics
Albuquerque, New Mexico
March 6-8, 1985

March 1, 1985

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Effects of laser radiation on surfaces and coatings

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Abstract

A summary is given of the principal aspects of laser-induced damage to polished optical surfaces and dielectric, thin-film, high-reflectivity and antireflective coatings. Methods for producing porous antireflective surfaces and coatings and their damage properties are also reviewed. Finally, new areas of basic research to solve current and future problems are addressed.

Introduction

Laser-induced damage to optical component surfaces and thin-film coatings is almost invariably the limiting factor in the output energy or power of high power lasers.¹ Consequently, the laser damage thresholds of available materials and components have a major impact on the cost, design, and performance of large laser systems, such as those used for laser fusion research.² Laser-induced damage has been the subject of sustained theoretical and experimental research since the beginning of laser technology. The most complete report of this body of research is the published proceedings of the annual Laser Damage Symposium.³

Laser damage to nominally transparent materials results from absorption of energy by impurity or defect sites. Such sites are ordinarily less than one micron in diameter. In high quality, optical materials the density of absorbing inclusions may be $\lesssim 1 \text{ cm}^{-3}$, and typical surface densities on polished, optical surfaces and thin-film coatings are $\sim 100 - 1000 \text{ cm}^{-2}$. Energy absorbed from the laser pulse heats these small absorbing volumes to temperatures which are sufficient to cause fracture or melting of the surrounding material.

The sources of absorption depend on the substrate and coating materials, methods of preparation and also on the laser's wavelength and pulse duration. Due largely to this fact, the major portion of the work on laser-induced damage has been phenomenological; primarily reporting the fluence or intensity at which damage occurs in a given material of some specific preparation under irradiation by a particular laser. Although substantial improvements in damage threshold levels have been made over the past decade, continued progress will almost certainly require development or adaption of analytical instruments and techniques to accurately characterize materials, lasers and their interactions. This topic is further addressed in the last section of this paper.

This paper reviews damage mechanisms and materials of interest for Nd lasers (fundamental wavelength and harmonics) and rare gas halide lasers. These lasers have wavelengths of 248-1064 nm and typical pulse durations of 0.1-30 ns. Also, only damage to polished surfaces of transparent dielectrics and dielectric coatings is discussed here. Internal, or bulk damage is covered elsewhere in these proceedings.⁴

Mechanisms and properties of damage

The composition and distribution of damage-inducing inclusions strongly affect the character of the damage threshold. Some surfaces and coatings have a well defined damage threshold; with catastrophic damage occurring when the laser's fluence is 5-10 percent above the fluence which first produced damage. Other surfaces have only slight or even no increase in degree of damage when irradiated at fluence levels up to two or three times above the initial damaging fluence.

Since damage arises from impurities, thresholds of apparently identical surfaces or coatings can vary widely, often by a factor of two. Thus, to test whether any new material or preparation offers improved damage resistance, a number of samples which is large enough to determine the distribution of thresholds must be measured.

Damage thresholds generally increase with increasing duration of the laser pulse. However, the functional dependence on pulse duration is different for various polished surfaces, coatings, and methods of preparation.⁵⁻¹¹ The most rapid increase in threshold observed is proportional to the square root of pulse duration. This behavior is characteristic of bare polished surfaces and some of the porous antireflection surfaces and coatings discussed in a later section. For most coatings, the thresholds increase more slowly with pulse duration and in some cases are constant over the 0.1-10 ns (or more) range of pulse durations. For sufficiently long pulses, some increase in threshold fluence is expected due to heat conduction away from the absorbing sight.

Many papers have discussed the dependence of damage thresholds on the diameter of the irradiated spot. It is now accepted that when the spot diameter is larger than the distance between easily damaged impurities, the threshold is independent of spot diameter.⁵ When the beam diameter is smaller than the distance between inclusions, it is, of course, possible to irradiate an area not containing an impurity and to infer a high threshold. Then, however, the threshold will vary widely over the surface, with lowest measured values equal to the large-spot threshold.

Damage thresholds do not depend strongly on the laser's wavelength in the near-IR and visible spectrum. Thresholds generally decrease with wavelength in the UV; probably due to the onset of absorption by most impurities in this spectral region.^{5,6,12-15}

Detection of damage

During laser irradiation of surfaces or coatings, several effects can be observed. Light may be emitted by an ionized plasma formed above the surface or by fluorescence. Emission of charged particles, neutral particulate plumes and generation of acoustic waves may also be observed. After irradiation, there may be changes in light scattered by the surface or morphological changes observable by optical or electron beam microscope. Table 1 summarizes the reliability of these various effects in defining a damage threshold which is a practical, operating fluence limit. Tests are rated as reliable (R), with the number giving orders of preference; unreliable (U), or either time consuming or too difficult (D) for routine usage. The difference between emission of light and sparks is that the later extend away from the irradiated surface.

Damage to optically polished, uncoated surfaces

Damage to entrance and exit surfaces of a transparent sample have different morphology, and the threshold fluence for exit-surface damage is lower than the entrance-surface threshold. Crisp et. al.¹⁶ explained that the threshold differences arise from interference between the incident and reflected electric fields, which are in phase and therefore add coherently at the exit surface, and are out of phase and subtract at the entrance surface. The ratio of exit- to entrance-surface fluence in a material of refractive index n is $4n^2/(n + 1)^2$.

Bare-surface damage is accompanied by avalanche ionization, which forms a dense plasma at the surface. This plasma reflects light and shields the front surface from further damage after the initial breakdown. At the rear surface, light is reflected back onto the surface, further increasing the laser's intensity and the extent of damage.¹⁷ Thus, front surface damage consists of shallow, rounded depressions which are difficult to observe with an optical or electron microscope. Rear surface damage morphology is that of well defined conical pits. Fig. 1 shows exit-surface damage to BK-7 borosilicate glass irradiated with 1 ns, 1064 nm laser pulses at fluences of 19, 25, and 37 J/cm², where the threshold damage fluence is 16 J/cm². Both the density of conical pits and their size increase with fluence.

For 353 nm wavelength pulses obtained by third harmonic generation of Nd lasers, the damage thresholds of fused silica move to lower values as shown in Fig. 3; with a median of 10 J/cm² for 0.6 ns pulses. All other glasses so far tested have exhibited nonlinear absorption or solarization at intensities above 2 GW/cm² for 353 nm wavelength.¹⁹

Damage thresholds of fused silica for KrF laser pulses (248 nm, 20 ns) are similar to those shown in Fig. 3.

The variation in 1 ns, 1064 nm damage thresholds of BK-7 glass and fused silica samples is shown in Fig. 2. The surfaces were prepared by state-of-the-art grinding and polishing procedures, in which residual, subsurface fracture is minimized by material removal at each polishing step to a depth on the order of three times the median diameter of polishing compound particles used in the preceding step.¹⁸ No systematic differences were found in thresholds of BK-7 and fused silica. The range in thresholds of roughly a factor of two for identically prepared surfaces is typical for both bare and coated surfaces.

Damage to dielectric coatings

Multilayer, dielectric, thin-film coatings used to reduce or enhance surface reflectivities consist of layers of two or more materials with different refractive index. The high- and low-index materials are deposited in alternate layers whose thickness is chosen to produce addition or cancellation of reflections from the interfaces between layers. Typical designs for high reflectivity (HR) and antireflective (AR) coatings are shown in Fig. 4, with the high-index layer shaded. The standing-wave electric field intensity of the laser light (normalized to the incident intensity) is superimposed on each design.

High reflectivity coatings

Damage to HR coatings normally occurs at the electric field maximum in the first or second outermost layer pairs because the laser energy is concentrated there, as shown by the standing-wave fields in Fig. 4. The optical thickness of each layer of the HR coating design in that figure is a quarterwave of the wavelength for maximum reflectivity. Attempts to increase HR damage thresholds by changing layer thicknesses to move the electric field maxima away from layer interfaces have had mixed success.²¹⁻²⁴ The addition of a halfwave thick overcoat layer of the low-index material on top of the HR stack increased the median damage threshold of $\text{SiO}_2/\text{TiO}_2$ HR coatings for 1064 nm wavelength lasers, as shown by Fig. 5, and also of $\text{Sc}_2\text{O}_3/\text{MgF}_2$ HR coatings for the 248 nm wavelength KrF laser.²⁵ However, for HR coatings of these and other materials when tested with 353 nm, 0.6 ns pulses, overcoat layers were ineffective in improving thresholds.²⁴ There is no generally accepted explanation for the effects of overcoats or for these observed differences.

The variation in damage thresholds among HR coatings composed of different combinations of high- and low-index materials is shown in Fig. 6. Four coatings of each material combination were made; two in each of two coating runs. Each coating had a minimum of 15 quarterwave-thick layers and was overcoated with a halfwave-thick layer of the low-index material. The materials used in these coatings were also damage tested as single layers.²⁶ An interesting, but not understood, fact is that the highest HR coating thresholds were considerably higher than thresholds of the single layers of the high-index material, and considerably lower than thresholds of the low-index material.

Antireflective coatings

AR coatings usually damage at lower fluences than HR coatings of the same materials and, in contrast to HR coatings, the damage usually originates at the interface between the substrate and first coating layer, as shown by Fig. 7. The photographs in this figure, taken by a scanning electron microscope, show individual damage pits of $3\mu\text{m}$ diameter inside the 2 mm diameter spot irradiated by the laser. The coating was $\text{SiO}_2/\text{TiO}_2$ of the four layer design shown in Fig. 4. The sequence of photographs (a)-(d) show the progression of damage with increasing fluence. Damage appears to result from a small, very hot spot at the substrate interface. The intense heat melted the glass substrate and the expansion created pressure which cracked and blew the overlying coating out of the crater. The sudden release of pressure ejected molten glass from the crater, where it quickly solidified.

Halfwave thick undercoat layers of low-index material, usually silica, deposited between the substrate and AR stack has been shown to increase damage thresholds.⁵ But, as with overcoat layers, there is no accepted explanation for this result.

Typical distributions of damage thresholds for $\text{SiO}_2/\text{TiO}_2$ AR coatings for 1064-nm, 1 ns pulses is shown in Fig. 8. The same coatings were deposited on substrates polished by different methods. The difference in thresholds is to be expected because, in AR coatings, the electric fields penetrate to the substrate, as shown in Fig. 4.

The influence of coating deposition parameters on laser-damage thresholds of $\text{SiO}_2/\text{Ta}_2\text{O}_5$ AR coatings, measured with 1064 nm, 1 ns pulses, is shown in Table 2. This series of 4-layer coatings was

deposited under 18 different combinations of substrate temperature, oxygen pressure, and rate of deposition. Damage thresholds for 1064 nm, 1 ns pulses were measured, as well as average absorption and net stress. Damage thresholds were not directly related to the average absorption or net stress. Baking the coatings in air for 4 h at 400 C generally reduced average absorption and stress, changed stress from compressive to tensile and, in some cases, increased the damage threshold.²⁷

Damage thresholds of coatings of various materials for 353 nm, 0.6 ns pulses are shown in Fig. 9. A wider variety of materials have been tested with results also in the 2-3 J/cm² range.²⁸

Porous antireflective surfaces and coatings

Reflection of light with wavelength λ from a surface, in air, of a material with refractive index n_s is eliminated by a layer of optical thickness $\lambda/4$ and index $n_c = \sqrt{n_s}$. For such single layer AR coatings on fused silica and other widely used optical glass with indices $n \sim 1.5$, the required coating index of $n_c = 1.22$ cannot be achieved by any fully dense (i.e. non porous) material. However, by introducing microscopic porosity, the refractive index of the surface layer or coating becomes $n_c = n_s V + (1-V)$ where the V is the volume fraction of remaining material. In addition, varying the volume fraction, or degree of porosity, produces a graded-index surface which can exhibit low reflectivity over a wide range of wavelengths and angles of incidence of light onto the surface.²⁹ Fig. 10 shows an example of the refractive index profile which can be produced by the methods discussed in this section.

The reduction of surface reflectivity of glass tarnished by exposure to acid was noted by Fraunhofer³⁰ and Rayleigh³¹ long before thin film coatings were developed for that purpose. Cook and Mader³² review the history of etching and leaching procedures for AR surfaces. The etching of phase-separated glass was shown by Minot³³ and later by Asahara and Izumitani³⁴ to provide antireflectivity throughout the visible and near-IR spectrum. Surfaces treated in this manner have damage thresholds 2-3 times higher than electron-beam evaporated, multilayer dielectric coatings.³⁵ However, phase-separated glass has scattering losses proportional to the fourth power of the light frequency and is thus impractical for lasers whose wavelengths are shorter than 500 nm.

To reduce this scattering loss, Schott Optical Inc., developed the Neutral Solution Process which produces AR surfaces on borosilicate glass, such as BK-7, without initial phase separation.^{32,36} The damage thresholds for these surfaces are also 2-3 times higher than electron-beam evaporated coatings as shown by Fig. 11. Both the phase-separated glass and Neutral Solution processes can produce porous AR surfaces only on materials with appropriate leachable components. Porous AR coatings which can be applied to a wider variety of substrate materials greatly increase the range of applications. Such coatings can be produced by "sol-gel" techniques in which single or multicomponent oxide films are deposited from solutions of metal organic compounds.

Porous silica AR coatings derived from acid-neutralized sodium silicate³⁸ and silica sols³⁹ have been used previously on glass substrates with varying effectiveness. These systems are aqueous and use

commercially available materials. Organic silicates in organic solvents as the silica source have also been studied.⁴⁰⁻⁴³ These volatile liquids are easily purified by fractional distillation, with the resulting silica, obtained by hydrolysis, retaining the high purity level and thus minimizing laser-induced damage.

In more recent work using tetraethyl orthosilicate (TEOS), coatings with high damage thresholds have been achieved.⁴⁴ The hydrolysis of TEOS requires an acidic or basic catalyst with the resulting products different in each case as illustrated by Fig. 12. With an acid catalyst, a soluble poly-ethoxysilane is first formed. A coating can be applied by dipping or spinning the substrate. Subsequent heating to 450 C to decompose organic material followed by a mild HF acid etch gives a porous AR coating.⁴³ However, the coatings formed in this process have generally low damage thresholds ($\sim 1 \text{ J/cm}^2$ for 353 nm, 0.6 ns pulses) possibly due to carbonaceous residue left in the coating.⁴⁵ The use of a basic catalyst produces a colloidal suspension of silica particles. These particles are deposited in solution and then dried to form an AR coating with no further treatment.

The transmittance of fused silica coated in this manner is shown in Fig. 13. Thicker coatings, which have transmittance peaks at longer wavelengths, are obtained by multiple, thinner coatings with air drying between each coating. The transmittance spectra are characteristic of quarterwave-thick homogenous coatings rather than graded-index surface layers.

The damage thresholds of these coatings, given in Table 3, are very encouraging. Note particularly the threshold of $8.5\text{-}10 \text{ J/cm}^2$ for 353 nm, 0.6 ns pulses. Comparing with Figs. 3 and 9 shows these coatings

have thresholds equal to that of bare, fused silica surfaces and are three times higher than vacuum deposited, multilayer AR coatings for this wavelength.

Basic research areas to solve current and future problems

The effects of laser radiation on surfaces and coatings and development of improved materials and deposition procedures has been to date approached mainly by empirical methods. Further progress will require a more systematic, scientific characterization. Included among areas for fruitful investigation are:

Identifying the fundamental causes of high absorption in thin films

This program should include development of analytical instruments and techniques to identify localized impurities and inclusions with spatial resolution of less than one micron. In addition, these instruments should also have the capability to profile impurity compositions as a function of depth into the surface or coatings. Also, a nondestructive method to identify and/or remove impurities during coating deposition would be of great utility.

Developing improved theoretical and experimental understanding of damage mechanism

In addition to single pulse damage, the effects of multiple pulses at various repetition rates and pulse durations should be understood.

Investigating alternate methods of polishing or subsequently treating optical surfaces

Various processes have been observed to greatly influence damage thresholds, and should be systematically investigated. Processes of interest include acid etching between polishing steps, use of a CO₂ laser to "fire polish" surfaces,⁴⁶ the effect of polishing compound composition and impurities as well as the mechanochemical aspects of polishing.⁴⁷

Developing alternate deposition technologies

With the exception of sol-gel coatings, virtually all coatings tested and used in high power lasers have been deposited by standard, electron-beam evaporation techniques. Within the past few years a variety of new deposition methods have been introduced or adapted for optical coatings. These methods include ion-assisted or laser-assisted electron-beam evaporation, ion-beam sputtering, molecular beam epitaxy and chemical vapor deposition. Although initial tests of the damage performance of coatings deposited by these methods have not shown significant improvement, an in-depth evaluation may lead to advances in coating performance.

Understanding laser conditioning of surfaces

It has been shown in certain cases that irradiating surfaces or coatings with laser pulses at fluence levels below those which produce damage by a single shot increases the damage threshold. This effect has been observed on bare surfaces of fused silica, Neutral-Solution Processed AR surfaces on BK-7 glass⁴⁸ and even for internal damage to KDP crystals.⁴⁹

Conclusion

Laser-induced damage is a persistent and serious problem affecting the design, cost and performance of high-power laser systems. Substantial improvement in damage thresholds of optical surfaces and coatings have been achieved by empirical methods. The outstanding example of such success is the development of sol-gel processes for porous AR coatings. In the future, more systematic study of damage mechanisms, surface processing and coating deposition methods will be required to continue improvement in the performance capability of large laser systems.

Acknowledgements

Many people have contributed to the work summarized here, which makes acknowledging each one impractical. It is my intent that their contributions be properly recognized by the references cited; with apology for the inevitable omission. I am particularly indebted to David Milam and Ian M. Thomas. Their diligence and creativity made possible much of the recent progress discussed here. Work performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract No. W-7405-ENG-48.

Table 1

Comparison of techniques for detecting threshold-level 1064 nm laser-induced damage to optical surfaces. Techniques practiced as described in the text are rated as reliable (R) or unreliable (U), and reliable techniques are ranked in order of preference. Some techniques are useful, but difficult (D) to employ. From Lowdermilk and Milam.⁵

<u>Technique for Detecting Threshold Damage</u>	<u>Single-Layer thin films</u>	<u>Thin-film AR coatings Thin-film polarizers</u>	<u>Thin-film Reflectors</u>	<u>Bare Glass Surfaces</u>
Nomarski microscopy	R-1	R-1	R-1	R-1
Increase in scatter	R-2	R-2	R-2	R-4
SEM microscopy	D	D	D	D
Bright-field microscopy	U	U	U	U
Dark-field microscopy	D	D	D	D
Emission of light	U	U	R-4	R-3
Emission of sparks	U	U	U	R-3
Breath fogging	U	U	R-3	R-2

Table 2

Damage thresholds (1064 nm, 1 ns) of Ta₂O₅/SiO₂ AR coatings with halfwave silica undercoats. Coatings were deposited by electron beam evaporation on bowl-feed polished fused silica substrates at three substrate temperatures, three oxygen pressures, and two deposition rates. From Milam *et. al.*²⁶

Deposition Rate (A/s)	O ₂ Pressure (Torr)	Substrate Temperature of 175°C		Substrate Temperature of 250°C		Substrate Temperature of 325°C	
		Sample	Threshold (J/cm ²)	Sample	Threshold (J/cm ²)	Sample	Threshold (J/cm ²)
1.5	0.5 × 10 ⁻⁴	A-1a	13.0 ± 3.0	A-4a	7.1 ± 0.7	A-7a	6.6 ± 0.7
		A-1b	9.6 ± 1.0	A-4b	6.6 ± 1.0	A-7b	6.8 ± 1.0
		B-1	9.0 ± 1.4	B-4	5.7 ± 1.3	B-7	3.5 ± 0.4
1.5	1.0 × 10 ⁻⁴	A-2a	18.7 ± 1.9	A-5a	6.9 ± 0.7	A-8a	4.7 ± 0.5
		A-2b	14.9 ± 1.5	A-5b	8.0 ± 0.8	A-8b	8.1 ± 0.8
		B-2	10.3 ± 1.0	B-5	6.1 ± 1.4	B-8	6.3 ± 0.7
1.5	2.0 × 10 ⁻⁴	A-3a	12.9 ± 1.4	A-6a	6.7 ± 0.7	A-9a	6.6 ± 0.7
		A-3b	9.5 ± 1.5	A-6b	11.0 ± 1.1	—	—
		B-3	11.1 ± 1.2	B-6	7.3 ± 0.9	B-9	5.8 ± 0.9
5.0	0.5 × 10 ⁻⁴	A-10a	7.1 ± 0.8	A-13a	2.2 ± 0.3	A-16a	1.8 ± 0.6
		A-10b	6.8 ± 0.9	A-13b	3.0 ± 0.4	A-16b	—
		B-10	4.9 ± 1.3	B-13	6.0 ± 0.6	B-16	3.9 ± 0.5
5.0	1.0 × 10 ⁻⁴	A-11a	6.7 ± 1.0	A-14a	5.3 ± 0.5	A-17a	5.4 ± 0.7
		A-11b	6.9 ± 0.7	A-14b	8.0 ± 0.8	A-17b	5.5 ± 0.6
		B-11	9.0 ± 1.0	B-13	6.9 ± 0.9	B-17	5.9 ± 0.8
5.0	2.0 × 10 ⁻⁴	A-12a	11.3 ± 1.1	A-15a	9.5 ± 1.4	A-18a	6.5 ± 0.6
		A-12b	9.3 ± 1.2	A-15b	8.5 ± 0.8	A-18b	6.4 ± 0.6
		B-12	5.5 ± 1.0	B-15	5.1 ± 0.5	B-18	5.5 ± 0.8

Table 3

Laser damage thresholds.

<u>Laser</u>	<u>SiO₂ substrate</u>	<u>KDP substrate</u>
248 nm, 15 ns pulse	4 - 5 J/cm ²	
346 nm, 0.6 ns pulse	8.5 - 10 J/cm ²	> 4 - 5 J/cm ²
1064 nm, 1.0 ns pulse	10 - 14 J/cm ²	

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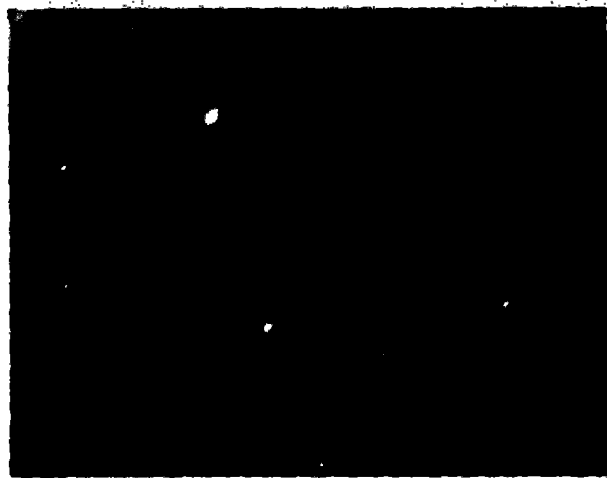
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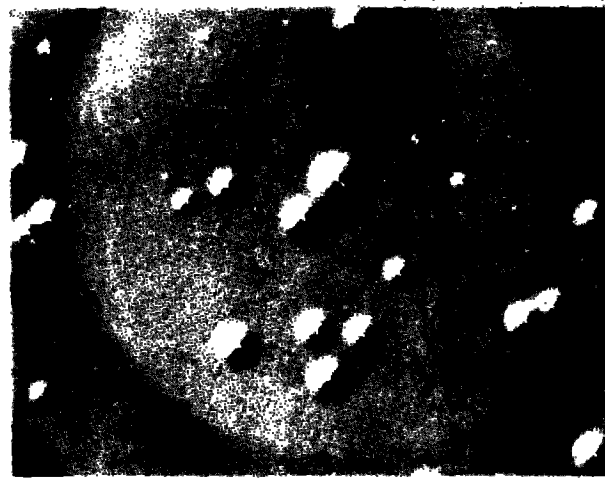
Figure Captions

1. Morphology of fused-silica exit-surface damage induced by 1 ns, 1064 nm pulses at fluence levels of (a) 19 J/cm^2 , (b) 25 J/cm^2 , and (c) 37 J/cm^2 . Threshold for surface damage was 16 J/cm^2 . Length of the white bar is $100\mu\text{m}$. From Lowdermilk and Milam.⁵
2. Distribution of damage thresholds of conventionally polished BK-7 glass and fused-silica surfaces measured with 1064 nm, 1 ns pulses. From Lowdermilk and Milam.⁵
3. Front-surface damage thresholds measured with 353 nm, 0.6 ns on 12 fused silica samples polished by one vendor. From Staggs and Rainer.²⁰
4. Designs for (a) AR and (b) HR coatings. High-index layers are shaded, and standing-wave electric-field intensity distributions are superimposed on the coating design. Field distributions are normalized to the incident intensity.
5. Distribution of damage thresholds of 15-layer $\text{SiO}_2/\text{TiO}_2$ quarterwave HR coatings (a) without and (b) with halfwave silica overcoat measured with 1064 nm, 1 ns pulses. From Lowdermilk and Milam.⁵
6. Laser damage thresholds (248 nm, 20 ns) of quarterwave-stack multilayer highly reflecting coatings made from 13 combinations of high-index and low-index materials. From Rainer et. al.²⁶
7. Morphology of damage to a four-layer $\text{SiO}_2/\text{TiO}_2$ AR coating. The laser pulse fluence increased from (a) to (d). Width of each photographed region is $3\mu\text{m}$. From Lowdermilk and Milam.⁵

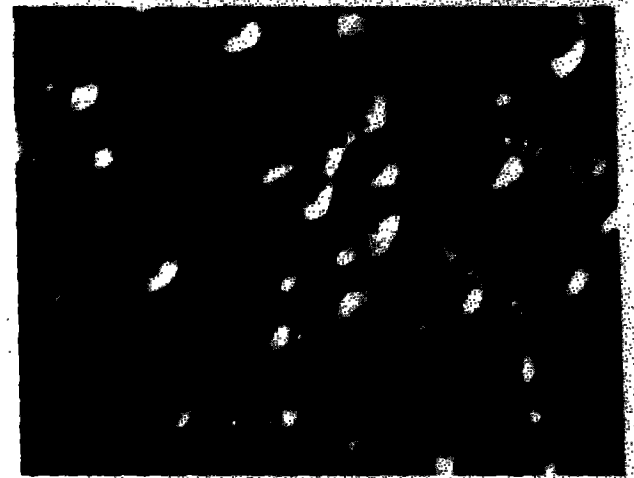
8. Distribution of damage thresholds of four-layer $\text{SiO}_2/\text{TiO}_2$ AR coatings deposited on (a) conventionally polished surfaces and (b) bowl-feed polished surfaces measured with 1064 nm, 1 ns pulses. From Lowdermilk and Milam.⁵
9. Laser-damage thresholds measured with 353 nm, 0.6 ns pulses on AR coatings that contain both low- and high-index materials. (*)Dual wavelength 248 nm, 353 nm coatings. From Tuttle Hart et. al.²⁸
10. Refractive index profile of a typical graded-index surface layer. From Lowdermilk²⁹
11. Histogram of laser damage thresholds for leached AR surfaces on BK-7 produced by the Neutral Solution Process and for $\text{SiO}_2/\text{TiO}_2$ thin-film AR coatings. Thresholds were measured with 1064 nm, 1 ns laser pulses. From L. M. Cook et. al.³⁷
12. Hydrolysis of tetraethyl silicate. From Thomas et. al.⁴⁴
13. Transmittance of coatings on fused silica substrates. From Thomas et. al.⁴⁴



(a)



(b)



(c)

Figure 1

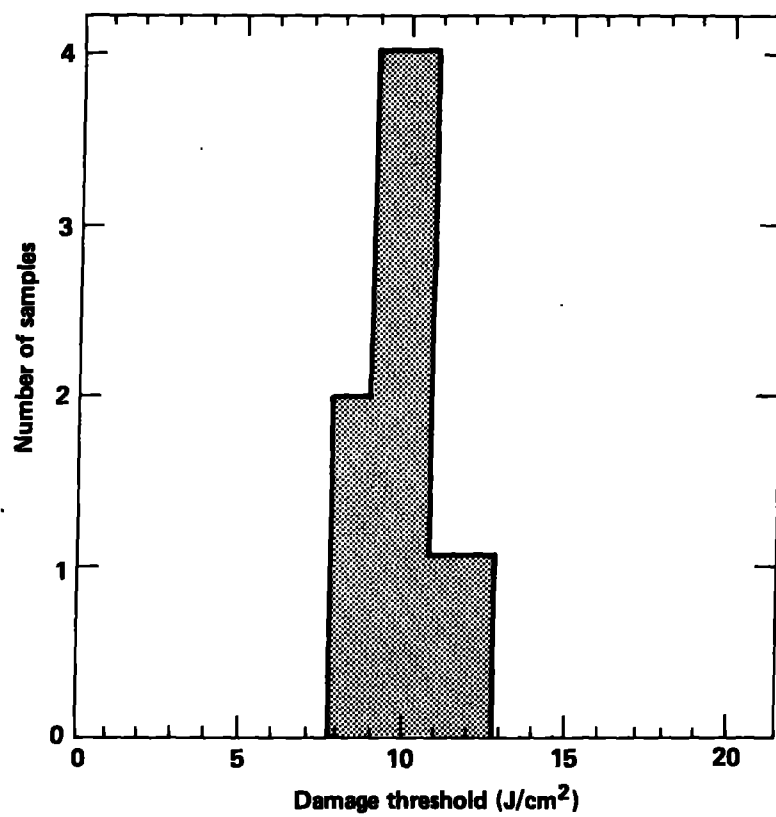


Figure 2

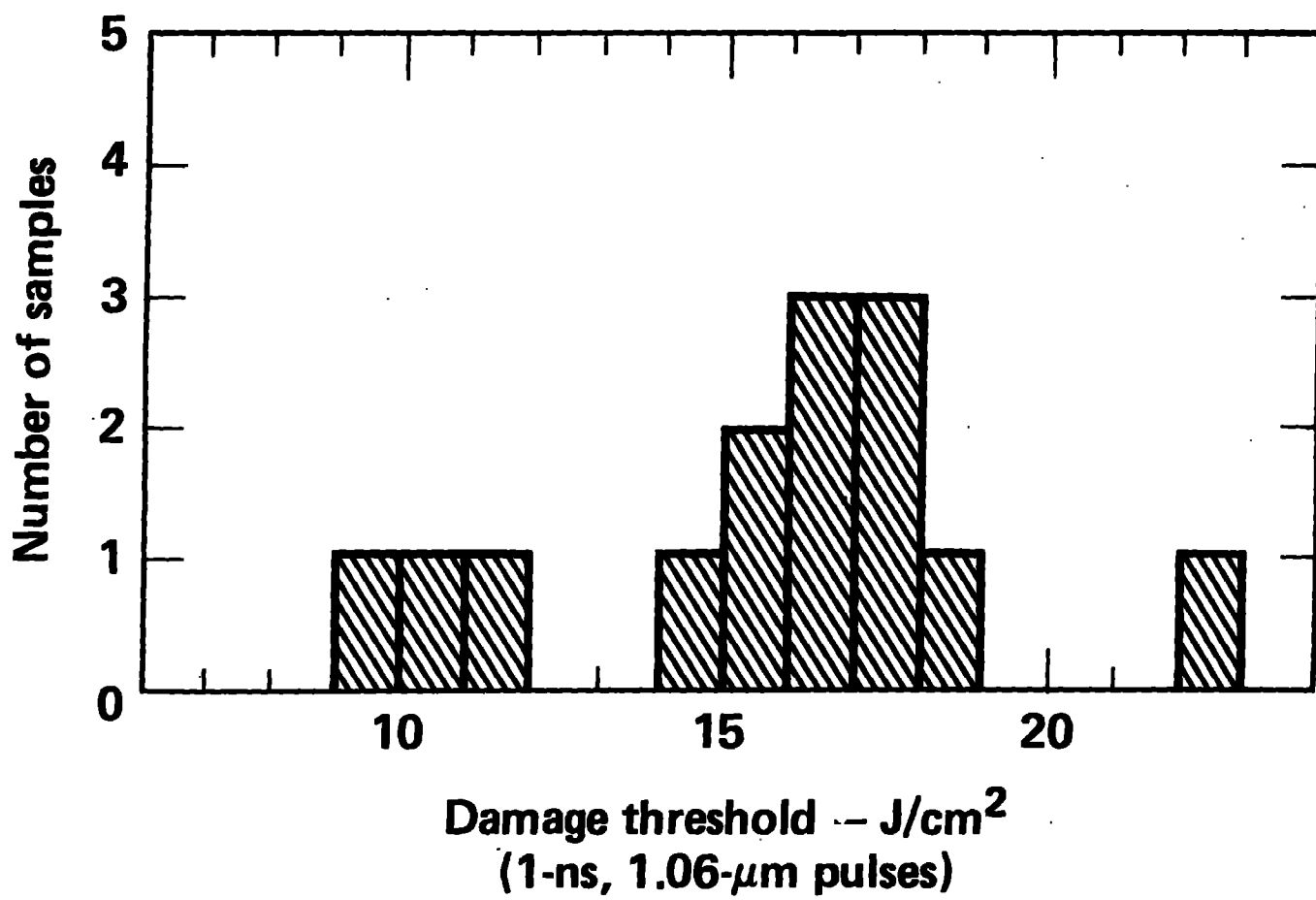


Figure 3

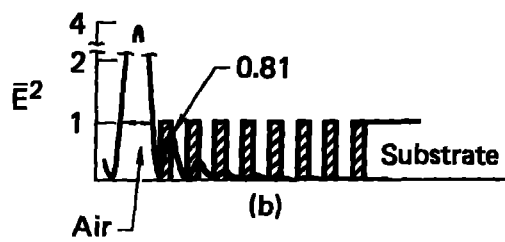
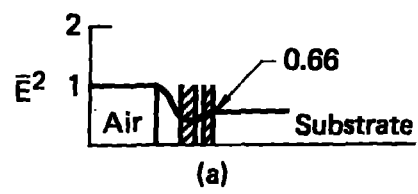
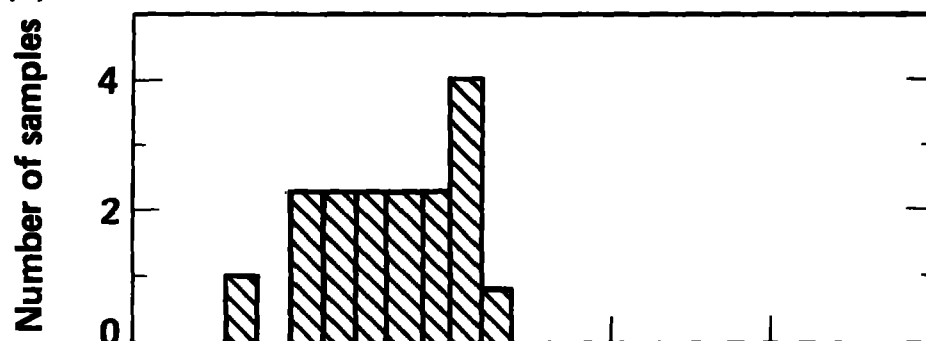


Figure 4

(a) Non-overcoated



(b) Overcoated

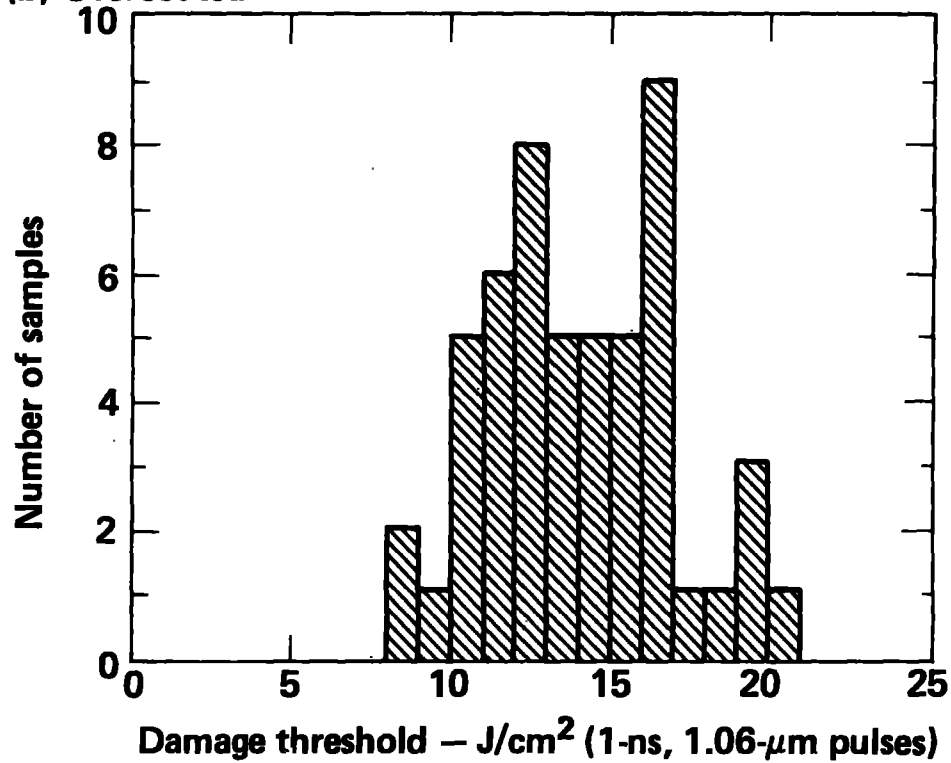


Figure 5

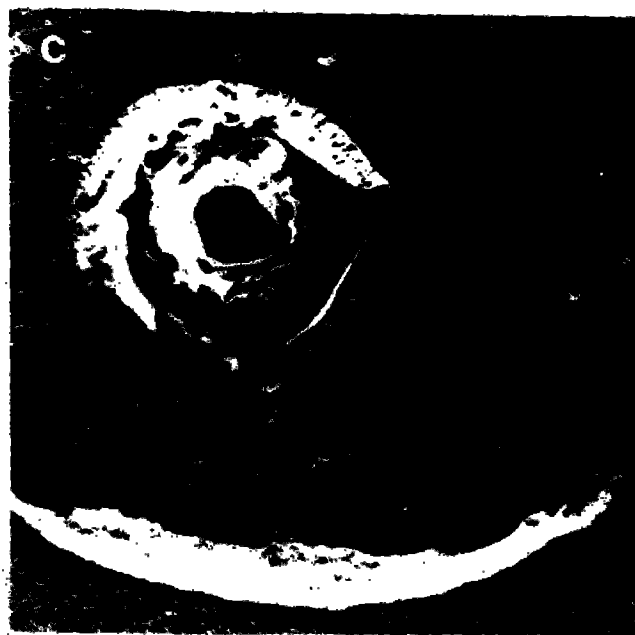
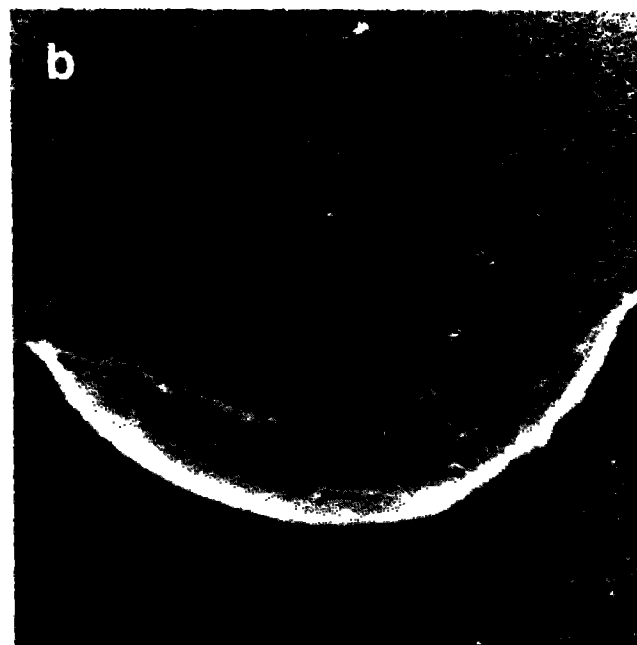
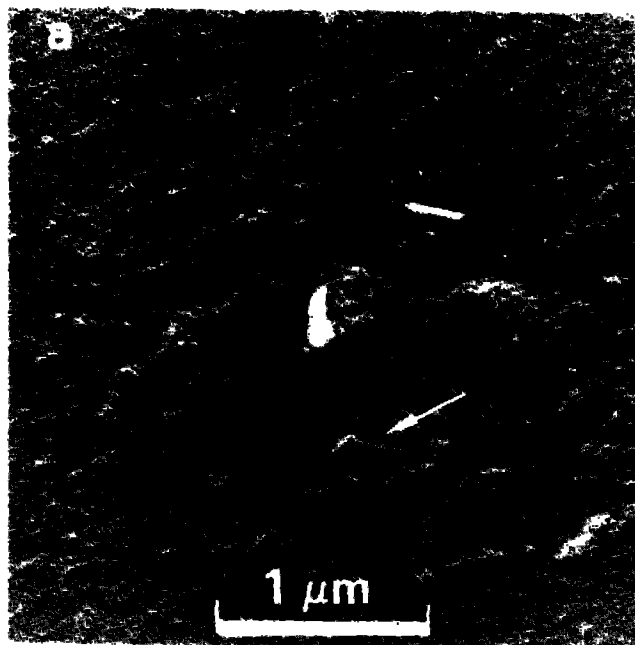


Figure 6

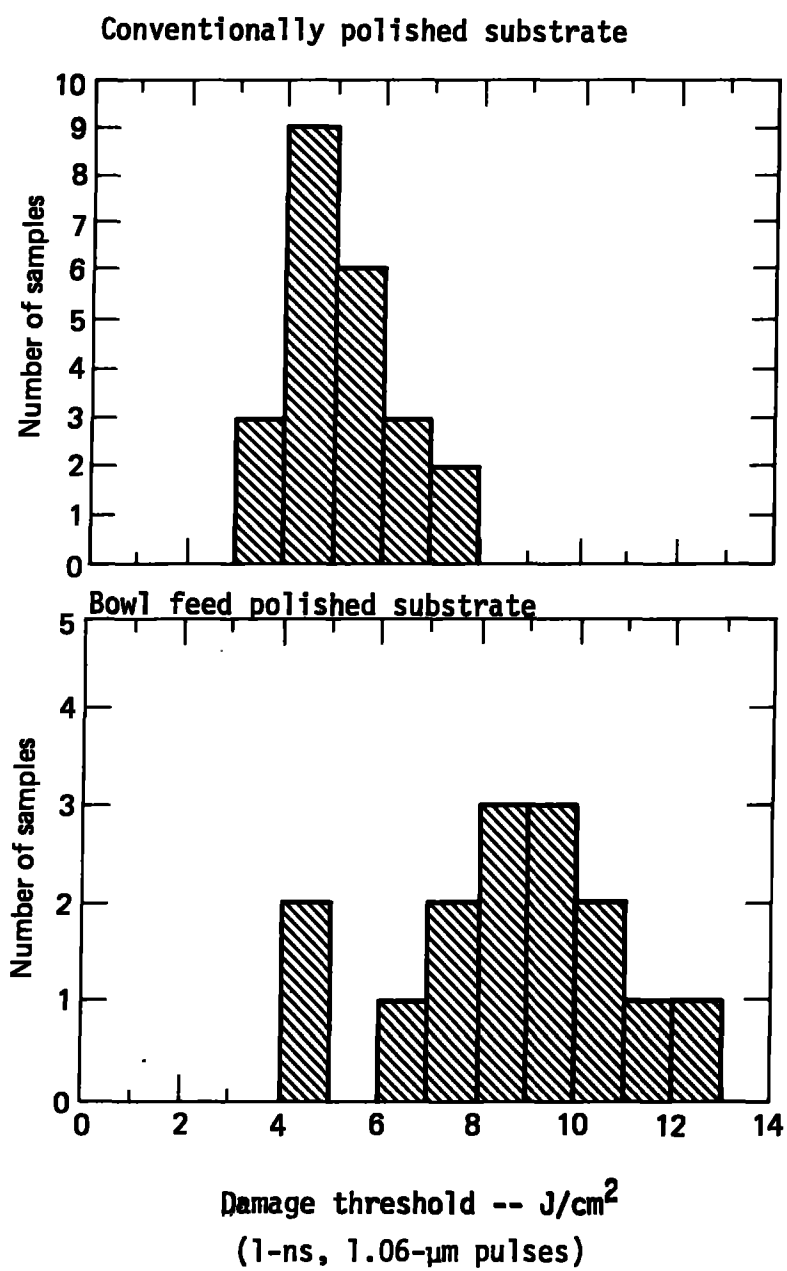


Figure 7

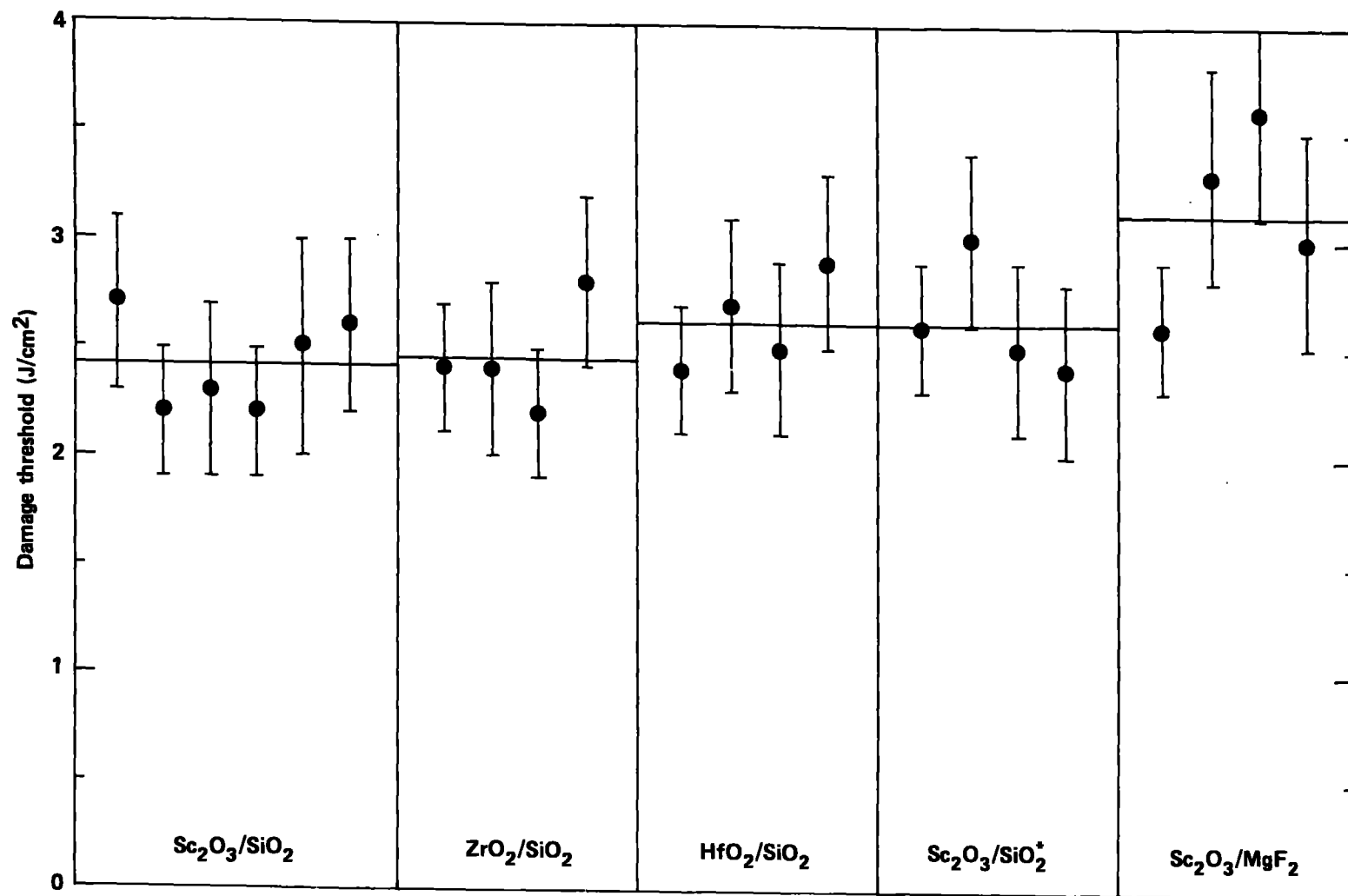


Figure 8

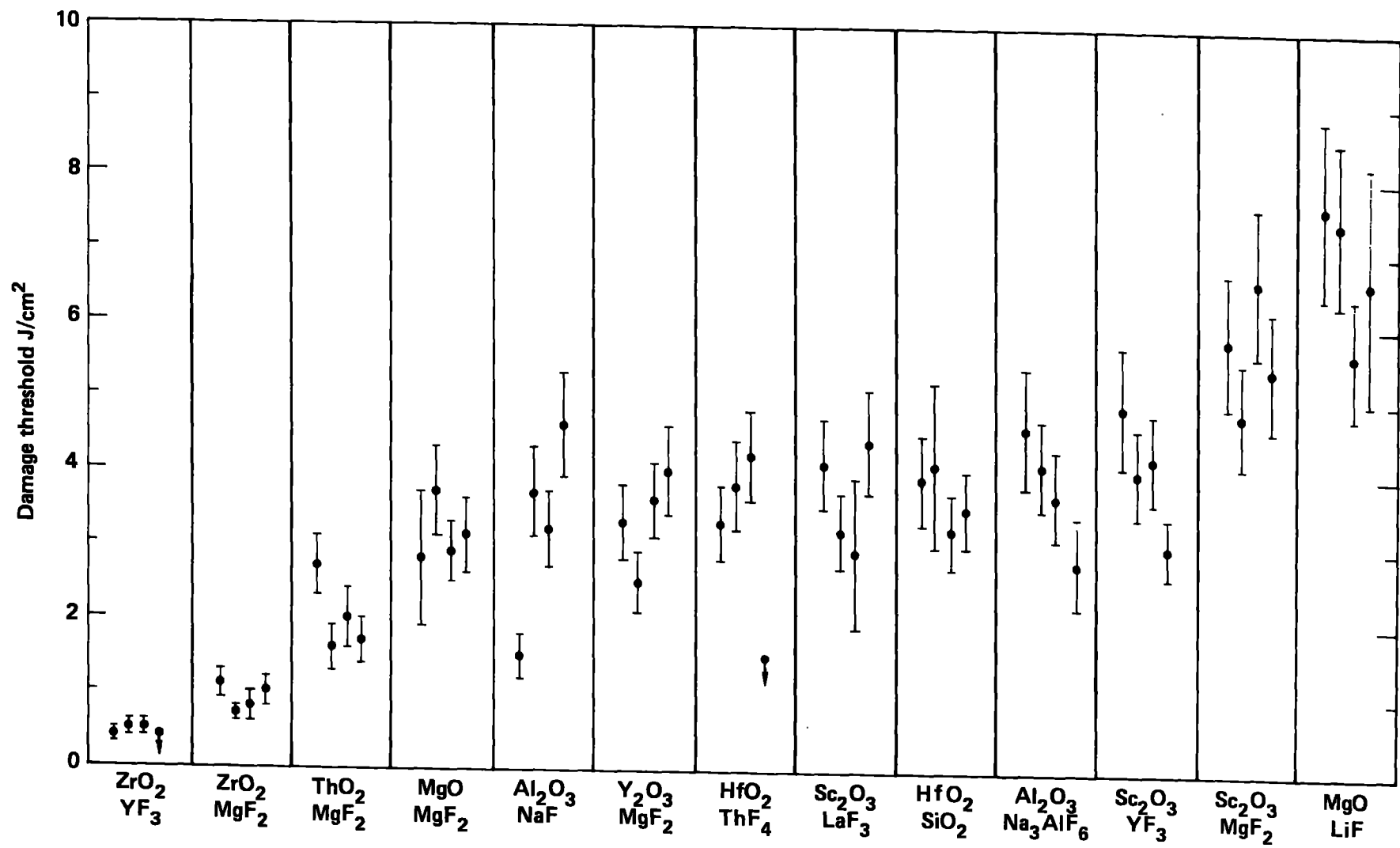


Figure 9

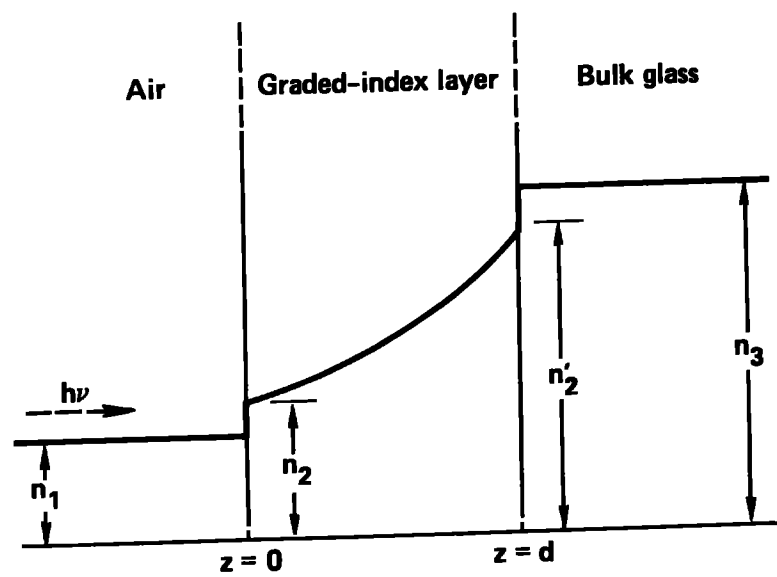


Figure 10

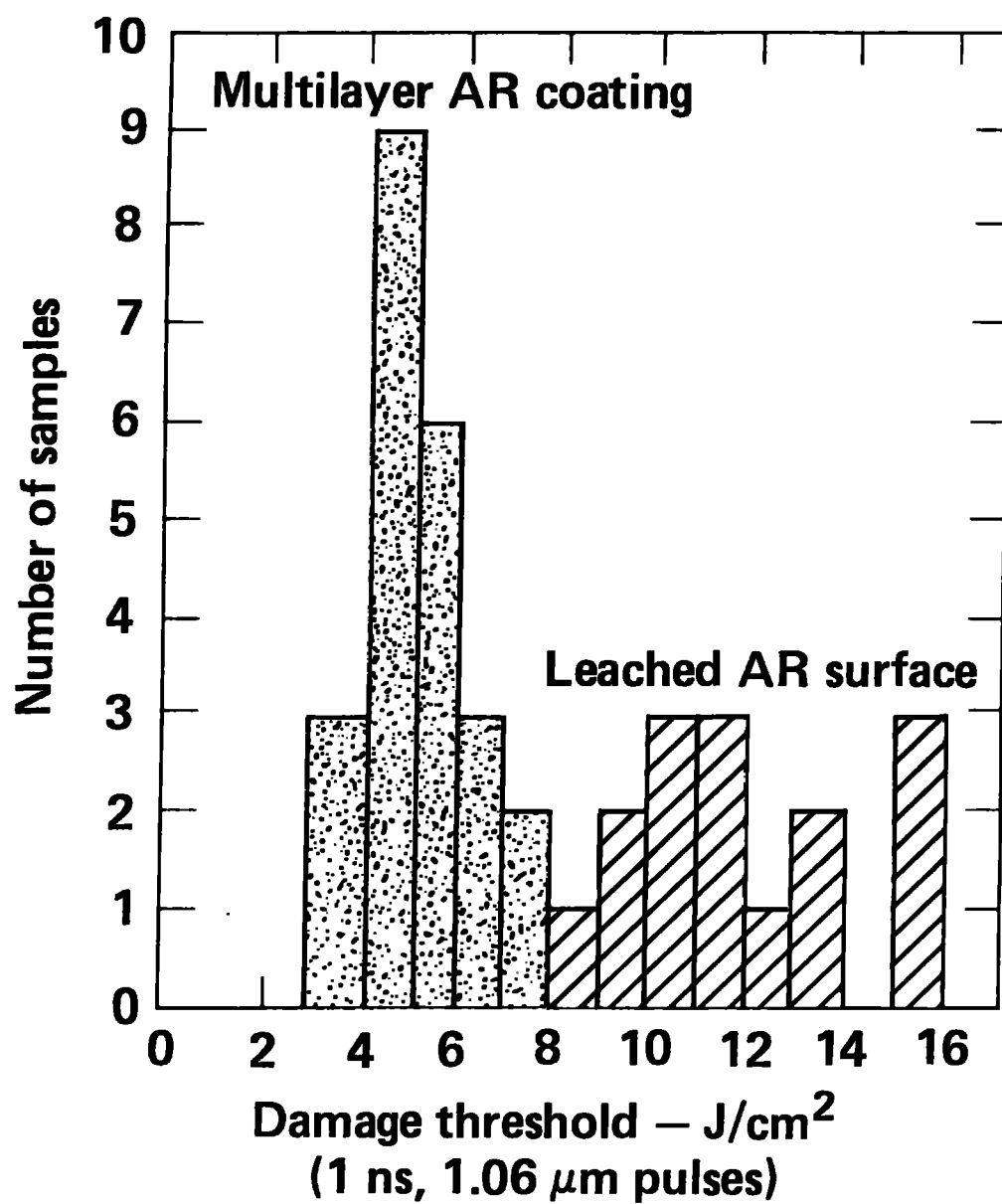


Figure 11

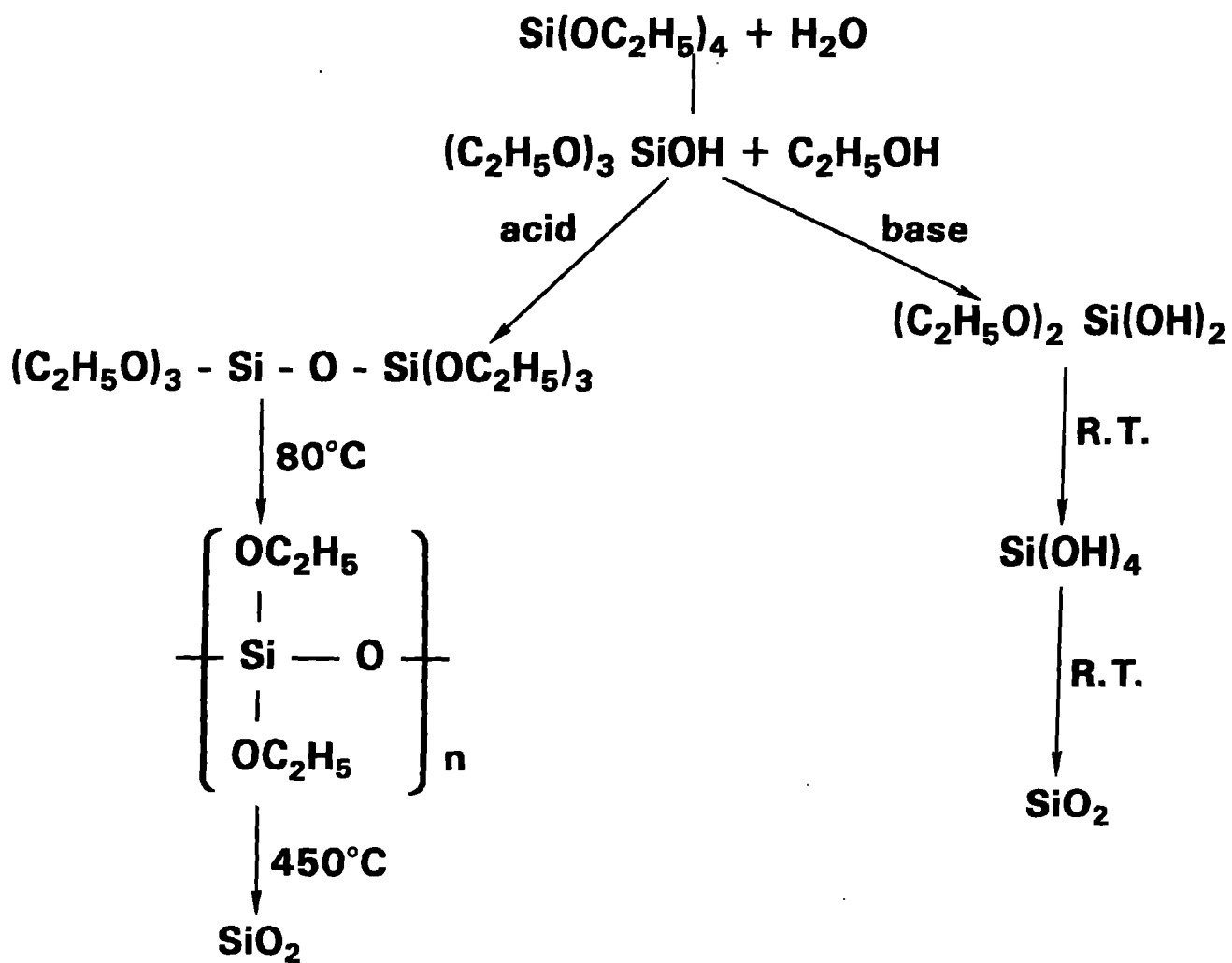


Figure 12

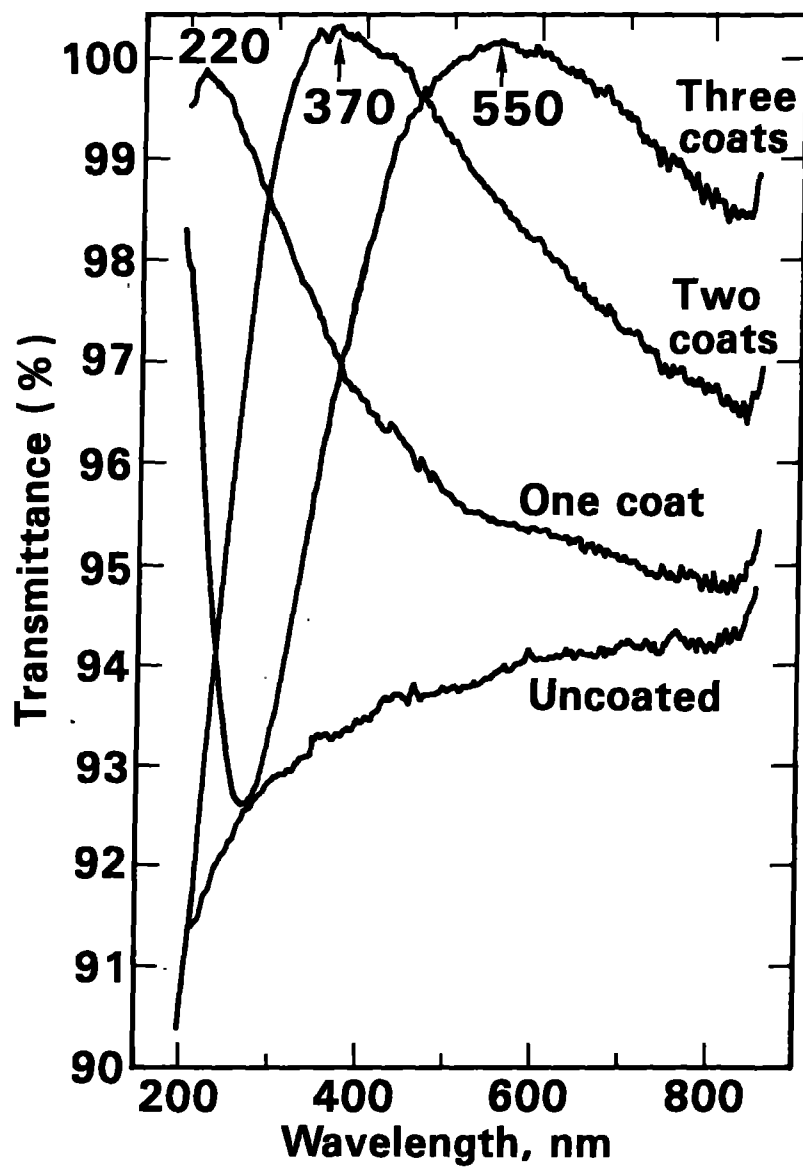


Figure 13